

Chains in critical fluids and nanopores

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The conformational behavior of a polymer in a critical binary solvent confined in a porous medium is studied. The size of the polymer in bulk, which is mainly governed by the correlation length of the solvent density fluctuations, depends on the proximity to the critical point of the binary mixture. We find that in contrast to the bulk behavior, the conformational properties of the polymer in a porous medium depends strongly on the pore size. The latter controls the correlation length of the solvent density fluctuations and thus determines the polymer size.

I. INTRODUCTION AND MODEL

The conformational behavior of polymers in a critical (binary) solvent is mainly governed by two length scales - the chain length and the correlation length of the solvent density fluctuations [1,2]. In particular, the size of a polymer in bulk is determined by the proximity to the critical point of the solvent mixture. Far away from the critical point, the size of a polymer in a binary mixture of good solvents simply scales as $R \sim N^{3/5}$, where N is the number of monomers. Close to the critical point, however, when the correlation length of the solvent density fluctuations is comparable to the chain size, the polymer collapses to form a globule of size $R \sim N^{1/3}$; a collapse transition close to the critical point is believed to be driven by the solvent density fluctuations which induce attractive interactions between different parts of the chain. At the critical point itself, when the solvent density fluctuations act on a much larger scale compared to the polymer size, the chain regains its original size, that is, $R \sim N^{3/5}$. These effects first studied by Brochard and De Gennes [2] using simple scaling arguments were later confirmed by simulations of Magda et al. [3], field theoretical and variational studies [1,4,5] and experiments [6–8].

The fact that the solvent density fluctuations are instrumental in determining the bulk behavior of polymers in a critical binary solvent raises an important question when such a polymer mixture is present in a restricted geometry, say a porous medium. Since the pore size affects the correlation length of the solvent density fluctuations and thus the polymer size, the question as to how a given confinement controls the conformational behavior of the polymer is an important one. This paper addresses this issue, which, we believe, has its implications in certain experimental situations like chromatography.

We begin by presenting a brief review of the bulk behavior — a self-avoiding polymer chain immersed in a binary solvent mixture, and describe it using the Edwards Hamiltonian formalism. The idea is to determine the effective potential exerted on a chain under various conditions of temperature and fluid composition. The Hamiltonian that describes the system of interest is given by

$$\begin{aligned} \beta\mathcal{H} = & \frac{3}{2b^2} \int_0^N \left(\frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds + \frac{1}{2}v \int_0^N ds \int_0^N ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \\ & + \sum_{\sigma=1,2} \sum_i v_\sigma \int_0^N ds \delta(\mathbf{R}(s) - \mathbf{r}_i^\sigma) + \beta\mathcal{H}_f, \end{aligned} \quad (1)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant and T the absolute temperature; $\mathbf{R}(s)$ is the chain variable, s the curvilinear coordinates along the chain (contour variable); the chain consists of N segments each of size b . The first term accounts for the connectivity of the chain and represents the chain entropy due to its elasticity. The second term results from two body interaction between monomers, where v is the strength of the bare monomer-monomer excluded volume interaction, which is assumed to be short ranged. The third term represents the interaction between the chain and the fluid in which v_σ is the strength of the short range excluded volume interaction between the monomers and the different species of the fluid. $v_1 \neq v_2$, i.e. the solvent quality is slightly different. In essence, it means that the chain is likely to be surrounded by solvent 2, when $v_1 > v_2$. $\beta\mathcal{H}_f$ describes the Hamiltonian of the fluid, the form of which needs to be specified. At this point we introduce a collective density field (order parameter) for the fluid, which is given by

$$c(\mathbf{r}) = \sum_{\mathbf{i}} \delta(\mathbf{r} - \mathbf{r}_{\mathbf{i}}), \quad (2)$$

which allows to rewrite the Hamiltonian in the simple form

$$\begin{aligned} \beta\mathcal{H} = & \frac{3}{2b^2} \int_0^N \left(\frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds + \frac{1}{2} v \int_0^N ds \int_0^N ds' \delta[\mathbf{R}(s) - \mathbf{R}(s')] \\ & + (v_1 - v_2) \sum_{\mathbf{k}} \int_0^N ds \exp[-i\mathbf{k}\mathbf{R}(s)] c(\mathbf{k}) + \beta\mathcal{H}_f(c(\mathbf{r})), \end{aligned} \quad (3)$$

where $\beta\mathcal{H}_f(c)$ can now be viewed as

$$\beta\mathcal{H}_f(c(\mathbf{r})) = \int d^3r \left(\frac{1}{2} (|\nabla c(\mathbf{r})|^2 + \tau c^2(\mathbf{r})) + \frac{\lambda}{4} c^4(\mathbf{r}) \right). \quad (4)$$

The parameter τ describes the distance from the critical point and λ is a coupling constant. Far away from the critical point the quartic term in Eq. (4) can be neglected, which amounts to $\lambda = 0$. The latter is a Gaussian approximation, which allows us to integrate out the solvent degrees of freedom to produce an effective interaction potential between different parts of the chain [1]. The effective Hamiltonian is given by

$$\beta\mathcal{H}_{\text{eff}} = \frac{3}{2b^2} \int_0^N \left(\frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 ds + \sum_{\mathbf{k}} \int_0^N ds \int_0^N ds' \tilde{v}(\mathbf{k}) \exp[-i\mathbf{k}(\mathbf{R}(s) - \mathbf{R}(s'))], \quad (5)$$

where

$$\tilde{v}(\mathbf{k}) = v - \frac{(\Delta v)^2}{\tau + (b\mathbf{k})^2} \equiv v - \frac{(\Delta v)^2}{(b/\xi_f)^2 + (bk)^2}. \quad (6)$$

In writing the above equation, we have defined $\Delta v = v_1 - v_2$. Since the (mean field) correlation length of the solvent density fluctuations is defined by $\xi_f \simeq b/\sqrt{\tau}$, the form of Eqs. (5) and (6) suggests that in certain temperature regimes depending on the strength of interaction between the chain and the fluid, the effective potential can become attractive (negative) to induce a chain collapse. In other words, depending on the correlation length of the solvent density fluctuations and Δv , the effective solvent quality can become poor. Therefore, before we discuss the problem of a chain in a restricted geometry, it is useful to briefly review the behavior of a chain in a nanopore under poor solvent conditions.

II. NANOPORES

A. Chains in Nanopores

Let us first review some of the scaling results of chains in nanopores. The diameter D of the tubes is assumed to be smaller than the natural chain radius $R_g \simeq N^\nu$, where in three dimensions $\nu = 1/2$ for theta-solvents and $\nu \approx 3/5$ for good solvents.

We consider flexible polymer chains confined in pores of cylindrical shape with neutral walls such that there is no adsorption between the polymer and the pores; the volume available to the solvent and the solute is limited by well defined boundaries. For the case of a single chain in a capillary of diameter D , there are two distinct behaviors depending on the dimensionless ratio R_F/D , where R_F is the Flory radius of a polymer in bulk. If $R_F < D$, we have a conventional bulk solution. If $R_F > D$ the chain is deformed and is confined in a cylindrical tube of diameter $D \ll R_F$. Since $D \gg b$, the chain still retains some lateral wiggling. We assume that the tube wall repel the chain strongly so that there is no trend towards adsorption. The length of the tube occupied by the chain is R_{\parallel} . The behavior of the chain can mainly be understood with the blob picture. The size of the blob is solely determined by the tube diameter. The parallel size of the chain is then made out of n_b blobs of diameter D such that $R_{\parallel} = n_b D$. The only information about the quality of the solvent is then in the number of blobs themselves, which is given by $n_b = N/g$, where g is the number of monomers inside a blob. The latter is simply given by $g = (D/b)^{1/\nu}$, and the size of the chain along the tube is $R_{\parallel} \simeq bN(b/D)^{(1-\nu)/\nu}$. Note that the same results can be derived by using a free energy as $\beta\mathcal{F} = R_{\parallel}^2/Nb^2 + \beta U$, where $\beta U \simeq b^3 N^2/D^2 R_{\parallel}$ for good solvents and $\beta U \simeq b^6 N^3/(D^2 R_{\parallel})^2$ for theta-solvents.

As discussed in the last section, the solvent density fluctuations can induce effective attractive interaction between different parts of the chain segments leading to a chain collapse. Since this amounts to the effective solvent quality becoming poor, it is worthwhile to consider the case of a polymer in a poor solvent confined in a nanopore. The free energy of such a system is given by

$$\beta\mathcal{F} \simeq \frac{R_{\parallel}^2}{Nb^2} - |v| \frac{N^2}{D^2 R_{\parallel}} + w \frac{N^3}{(D^2 R_{\parallel})^2}, \quad (7)$$

where $v \sim -tb^3$ and $w \sim b^6$ are the two and three body interactions respectively. Here the reduced temperature t describes the distance from the theta temperature, i.e., $t = |T - \Theta|/\Theta$. Let us first discuss the influence of the tube geometry on the Θ -point. To estimate the Θ -temperature, we employ the usual Ginzburg criterion. The Θ -point for a finite chain length in a restricted geometry cannot be defined by simply setting the second virial coefficient equal to zero. Instead, a consistent expression can be determined by the balance between the chain entropy and the attractive second virial term. In particular, when t is sufficiently large (the solvent quality is poor enough), the first term in Eq. (7), which represents the entropic elasticity, is smaller than the attractive interaction due to the second term. Thus the Θ -point for chains inside the pore can be determined by comparison between the entropic term and the negative second virial term. This yields the following condition for the Θ -point:

$$t \simeq (D/b)^2 (R_{\parallel}/bN)^3, \quad (8)$$

where the estimate is sensitive to the unperturbed chain size R_{\parallel} . The usual Ginzburg criterion uses the ideal chain size $R \propto bN^{1/2}$, but this yields the unphysical result $t_c \simeq (1/\sqrt{N})(D/bN^{1/2})^2$ since it suggests an increase in t with the increase in the pore diameter. Moreover, the chain length cannot play a significant role since the collapse in the pore takes place only on the length scales less than the pore diameter, i.e., the relevant blob size. Therefore, it is physical to use the Gaussian value for R_{\parallel} inside the pore, which is simply given by $R \simeq bN(b/D)$, as suggested by a simple blob argument. As a result, the value for the shift of the Θ -temperature is given by

$$t = \frac{b}{D}. \quad (9)$$

The above equation shows significant dependence of the Θ -temperature on the pore size. It can be rewritten as

$$\theta = \theta_{\text{bulk}} + \text{const} \frac{b}{D}, \quad (10)$$

which is only valid for $D \leq b\sqrt{N}$, i.e., when the pore diameter is smaller compared to the Gaussian chain size. When D becomes comparable to the chain size, then the shift of the Θ -temperature is determined by $t \simeq b/R_{\text{Gauss}}$, which is simply $t \propto 1/\sqrt{N}$, as it must be the case for the collapse of polymer chains in bulk. The geometry dependence of the Θ -temperature has recently been studied for a polymer confined between two parallel plates (slit geometry) by using numerical methods [12]. For completeness, we would like to remark that naive scaling for a simple slit geometry predicts $t_{c,\text{slit}} = (b/D)^0$, which suggests a logarithmic dependence, $t_{c,\text{slit}} \propto \log(D/b)$, but this needs further investigation.

For $t > t_c$ the chain becomes significantly contracted from its theta size. The stretching term can then be neglected, and the balance between the attractive and repulsive third body potential yields the chain size

$$R_{\parallel} \sim \frac{b}{t} N \left(\frac{b}{D} \right)^2. \quad (11)$$

The density inside the tube is simply given by $\rho \sim \frac{N}{D^2 R_{\parallel}} \simeq t/b^3$, which corresponds to the density of a unconstrained globule and also defines the thermal blob size $\xi_T = b/t$. On length scales smaller than ξ_T , the chain statistics are unperturbed by the volume interactions and are that of a random walk, i.e., $\xi_T \sim bg_T^{1/2}$. The parallel extension of the chain can, therefore, be expressed by comparing the blob size ξ_T and the diameter D ,

$$R_{\parallel} \sim bN \frac{\xi_T}{D} \left(\frac{b}{D} \right). \quad (12)$$

Using the above expression, the size of the polymer confined in a tube of diameter D can be summarized for three distinct cases: When $D < \xi_T$, the chain experiences theta conditions; when $D > \xi_T$, the chain inside the tube finds itself in a poor solvent condition. It collapses to form a globule of size governed by t . The chain starts to shrink when $D = \xi_T$, starting from the size $R_{\parallel} \sim bNt$, i.e., a linear arrangement of the thermal blobs.

B. Critical fluids in Nanopores

The problem of phase transitions in restricted geometry has been considered mostly in the case of (two dimensional) wetting. In a nanopore the situation is very different. The problem of a spherical model in a spherocylinder has been studied by Cardy [13], who shows using conformal mapping that the correlation length at the critical point can be written as

$$\xi^{-2} = A/D^2 \quad (13)$$

where $A = d - 2 + \eta$ is a universal amplitude; it depends only on the space dimension d and the critical exponent η . This result implies also that the amplitude and so ξ does not depend directly on the value of the fluid coupling constant λ , which was introduced in eq. (4). Physically, this implies that the criticality plays a significant role only on the scale of the tube diameter D and fluctuations always stay finite. Therefore, the effects of the solvent density fluctuations on the conformational behavior of a polymer chain, which is dissolved in a bicomponent solvent present in a porous medium, are mainly local. These effects are studied in the next section.

C. Polymer chain and fluids in nanopores

As discussed in the previous section, when the chain dissolved in a bicomponent solvent is confined in a nanopore, the problem is effectively one dimensional. To see this we can rewrite all spatial vectors in their Cartesian coordinates, that is

$$\begin{aligned} \beta\mathcal{H} = & \frac{3}{2b^2} \sum_{\mu=x,y,z} \int_0^N \left(\frac{\partial R_\mu(s)}{\partial s} \right)^2 ds + \frac{1}{2}v \int_0^N ds \int_0^N ds' \prod_{\mu=x,y,z} \delta[R_\mu(s) - R_\mu(s')] \\ & + (v_1 - v_2) \sum_{\mathbf{k}} \int_0^N ds \exp[-i \sum_{\mu=x,y,z} k_\mu R_\mu(s)] c(\mathbf{k}) + \beta\mathcal{H}_f(c(\mathbf{r})). \end{aligned} \quad (14)$$

Moreover, when the constraints due to the cylindrical geometry of the tube are imposed the effective potential remains structurally similar. Because of the confinement, the vector \mathbf{k} can be splitted into its Cartesian components, i.e., $\mathbf{k} = (k_\parallel, k_\perp, k_\perp)$, where k_\parallel corresponds to the length scale along the (cylindrical) tube. The component k_\perp is limited by the tube wall and can be replaced by its upper limit $1/D$. This naive estimate suggests that the effective potential is given by

$$\tilde{v}(\mathbf{k}) = v - \frac{(v_1 - v_2)^2}{(bk_\parallel)^2 + \tau + \left(\frac{b}{D}\right)^2}. \quad (15)$$

Within this mean field model, the new correlation length can be identified as

$$b^2\xi_{\text{tube}}^{-2} = \tau + \left(\frac{b}{D}\right)^2. \quad (16)$$

It is interesting to note that the scaling of the correlation length agrees with the exact result of Cardy [13] at $\tau = 0$.

To estimate the size of the chain within the classical scaling, it is sufficient to discuss the limit $k_\parallel = 0$. The effective potential can then be casted into a Flory form, which yields together with the Gaussian stretching term a reasonable estimate for the size of the chain. The effective potential is given by

$$\tilde{v} = v - \frac{(\Delta v)^2}{\tau + \left(\frac{b}{D}\right)^2}. \quad (17)$$

For $\tau = 0$, i.e., at the critical point this equation is similar to the corresponding mean-field equation in the bulk, Eq. (6) in the low wave vector limit. For geometrically unrestricted systems $D \rightarrow \infty$, the correlation length grows then with the pore diameter, because here we have $\xi_f \propto D$. At the critical point, i.e., $\tau = 0$, the effective monomer-monomer potential \tilde{v} becomes negative when the tube diameter is sufficiently large:

$$\left(\frac{D}{b}\right)^2 \geq \frac{v}{(v_1 - v_2)}. \quad (18)$$

Since this amounts to the effective interaction between the chain segments being attractive, the chain is expected to collapse inside the tube. In contrast to the bulk behavior, where in a certain temperature regime (close to the critical point) the chain is always collapsed, the collapse in a confined geometry depends purely on material properties — the strength of the polymer - fluid interaction, the chain excluded volume, and the diameter of the tube. The geometry, therefore, plays an important role in the collapse of a polymer chain both in a critical fluid and a fluid with a finite correlation length.

D. The size of the chain

The Hamiltonian as given by Eq. (5) can be transformed into a Flory free energy by simple dimensional analysis [11]. It has to be modified such that the 3-dimensional Dirac function is anisotropic and the lateral dimensions are determined by the diameter D of the nanopore. Thus, we can estimate the excluded volume to be $\delta(\mathbf{R}(s) - \mathbf{R}(s')) \propto 1/(D^2 R_{\parallel})$, where R_{\parallel} is the chain size parallel to the pore. The interaction parameter between the monomers is determined by the value for the effective chain potential $\tilde{v}(k_{\parallel} = 0)$:

$$\beta\mathcal{F} = \frac{R_{\parallel}^2}{Nb^2} + \tilde{v}(k_{\parallel} = 0) \frac{N^2}{D^2 R_{\parallel}} \quad (19)$$

Minimization of the above free energy yields the size of the chain in the nanopore:

$$R_{\parallel} \sim \left(v - \frac{(v_1 - v_2)^2}{\tau + \left(\frac{b}{D}\right)^2} \right)^{1/3} N \left(\frac{b}{D} \right)^{2/3}. \quad (20)$$

The above expression is valid as long as the effective potential is positive. At the critical point $\tau = 0$, we can use Cardy result for $d = 3$ and to get

$$R_{\parallel} \simeq bN \left(1 - \frac{1}{(1 + \eta)} \chi^2 \left(\frac{D}{b} \right)^2 \right)^{1/3} \left(\frac{b}{D} \right)^{2/3}, \quad (21)$$

where we have rescaled the interaction parameters by the size of the Kuhn length $v \sim b^3$ and introduced $\chi^2 = (v_1 - v_2)^2$. This results holds as long as the effective potential is positive, which means that the pore size is small enough. For larger pore sizes as

$$D > \frac{v}{(v_1 - v_2)^2}, \quad (22)$$

the effective potential becomes negative; the critical fluid then resembles a poor solvent. The size of the chain can then be estimated by taking into account the three body interaction in the tube. Its lateral extension is then given by

$$R_{\parallel} \propto N \frac{1}{(\chi^2 (D/b)^2 - 1)} \left(\frac{b}{D} \right)^2. \quad (23)$$

Therefore, the chain is always in a stretched conformation, as has already been seen from the scaling analysis of the behavior of chains in solvents of different quality.

III. APPLICATIONS AND DISCUSSION

The behavior of chains immersed in a critical fluid confined in a porous media is substantially different from the bulk case. As mentioned in the Introduction, a chain in bulk undergoes a conformational transition, i.e., $N^{3/5} \rightarrow N^{1/3} \rightarrow N^{3/5}$, on approach to the critical point of the fluid. In a restricted geometry, however, the correlation length of the fluid stays finite and is mainly determined by the typical size of the tube. The latter implies that the pore diameter can select chains according to their chain length — for a given pore diameter D , short chains (of size much less than D) are not restricted by the confinement; they can undergo a collapse transition on approach to the critical point, as is the case in the bulk. Sufficiently long chains (of size much larger than D), on the contrary, remain in a

stretched conformation. As a result, the variation in the fluid temperature, that is, approach towards its “criticality” can select chain conformations according to their polymerization degree.

To see this let us consider a dilute solution of chemically identical chains having degrees of polymerization N_1 and N_2 dissolved in a good solvent such that $N_1 \gg N_2$. In terms of the present model, a good solvent quality implies $\tau > \chi^2 - (b/D)^2$ (i.e. the temperature not too close to the critical point where $\tau = 0$). When the pore size is such that $D \sim N_2^{3/5}$, only long chains of size $N_1^{3/5}$ will be confined. The confinement free energy for the long chain is given by

$$\beta F \simeq N_1 \left(\frac{b}{D} \right)^{5/3}, \quad (24)$$

which is estimated as the number of blobs times $k_B T$. The free energy for the non-confined chain is roughly given by

$$\beta F \approx N_2 \log N_2 - (\gamma - 1) \log N_2. \quad (25)$$

where γ is the partition function critical exponent. The comparison of the two free energies yields

$$\frac{D}{b} \approx \left(\frac{N_1}{N_2} \right)^{3/5}, \quad (26)$$

which provides a simple scaling for the separation of chains according to their chain length. It is to be noted that in writing the above expression we have ignored the logarithmic dependence in Eq. (25).

Eq.(9) suggests another interesting possibility — the chain length dependence of the second virial coefficient allows us to determine the temperature away from the critical point where the separation between the collapsed short chains and the more stretched long chains occur:

$$\tau^* = \frac{\chi^2}{1 + (b/D)} - \left(\frac{b}{D} \right)^2. \quad (27)$$

For chains whose size is less than that of the pore diameter, the above condition suggests

$$\tau_N^* = \frac{\chi^2}{1 + 1/\sqrt{N}} \quad (28)$$

Thus by tuning the distance from the critical point, that is τ , the chains may adopt different (globular) conformation depending on their chain lengths. This provides a means for separating chains by changing the poor solvent quality (through the change in the criticality of the fluid) in porous media.

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